

## Article

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# Simulating Herbicide Volatilization from Bare Soil Affected by Atmospheric Conditions and Limited Solubility in Water

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A numerical model that simulates pesticide fate was developed to predict the behavior of triallate after application to a field soil. The model has options that allow water and/or heat transport and can limit simulated aqueous-phase concentrations to triallate solubility in water. Several methods for describing the volatilization boundary condition were tested to assess the accuracy in predicting the volatilization rate, including an approach that requires no atmospheric information and an approach that couples soil and atmospheric processes. Four scenarios were constructed and simulated, to compare with measured volatilization rates. The peak measured volatilization rate ( $168 \text{ g ha}^{-1} \text{ h}^{-1}$ ) was most accurately predicted with the scenario that included the most complex model ( $100 \text{ g ha}^{-1} \text{ h}^{-1}$ ). The simplest model overpredicted the peak rate ( $251 \text{ g ha}^{-1} \text{ h}^{-1}$ ), and the others underpredicted the peak rate ( $16\text{--}67 \text{ g ha}^{-1} \text{ h}^{-1}$ ). The simulations that limited aqueous solubility provided relatively similar values for the total emissions ( $21\text{--}37\%$  of applied triallate), indicating that simplified models may compare well with measurements ( $31\%$  of applied). A prospective simulation over a period of 100 days showed that applying triallate to the soil surface would ultimately lead to atmospheric emissions of  $80\%$  of the applied material with  $6\%$  remaining in soil. Incorporating triallate to a depth of 10 cm would reduce emissions to less than  $5\%$  and lead to  $41\%$  remaining in soil.

## Introduction

The use of pesticides in agriculture has become highly regulated due to concerns about public and environmental health. Studies have shown that pesticides used in agriculture can contribute to the contamination of water (1, 2) and the atmosphere (3–5). Many risk assessments involve predicting the fate and transport of pesticides after application. Often these approaches are limited to simple configurations and may neglect important environmental conditions. For volatile pesticides, emissions to the atmosphere is a significant dissipation pathway, and understanding this process is important in terms of improving pesticide efficacy and minimizing environmental contamination. Volatilization has the potential to contaminate the atmosphere and could cause an increased health risk to persons living near treated fields. This can be especially problematic since many pesticides, including triallate, are considered to be possible human carcinogens (6). It is known that volatilization is affected by

many interrelated factors such as pesticide application methods, water management practices, and soil and atmospheric conditions (3, 4, 7, 8). However, research that couples soil and atmospheric processes to emissions from soils is needed to develop more accurate methods to predict volatilization.

Simple models of pesticide fate and transport have been successfully used as screening tools and to categorize pesticides into groups based on chemical properties and transport behaviors. Jury et al. (9) described a screening model to assess relative volatility, mobility, and persistence of pesticides in the soil. Rao et al. (10) and Loague et al. (11) reported on retardation and attenuation factors, which categorize pesticides based on adsorption and degradation. These methods have allowed regulators to consider classes of chemicals and develop rational approaches to minimize potential adverse effects and to identify pesticides likely to become problems as usage shifts to new or alternative compounds with similar properties. While simple models provide valuable information, they do not provide accurate assessments of pesticide fate and transport under extreme and highly variable conditions common in large-scale agricultural settings. For example, simple methods do not provide accurate estimates of the short-term emission rate (12), and yet this information is very important in determining the risks of acute inhalation toxicity.

Field experimentation offers an alternative to the use of simulation for developing information in support of pesticide use and regulation. For example, volatile organic chemical (VOC) emissions have become a serious concern in California's interior valleys because of the new federal 8-h ozone standard. Reduction of VOC loading to the atmosphere can be achieved by reducing pesticide emissions from treated soil. However, currently California requires large-scale, time-consuming, costly, and complex experiments to provide information and performance measures for new emission-reduction methodology. These experiments are conducted at a specific site and time and are heavily influenced by the prevailing cultural practices, soil, and environmental conditions. This information is then used throughout California for regulation without regard to the applicability of the information at each particular location. Given the range in variability in soil, environmental, and cultural conditions throughout the state, it is unreasonable to expect that highly site-specific experimental information will represent realistic emissions at other locations and times.

Given the large number of factors affecting pesticide emissions from soil, vast investments of time and capital would be needed to study every possible scenario through field experimentation. It is clear that simple and cost-effective methodology is needed to assist the regulatory community in protecting public and environmental interests, while minimizing unnecessary impact to our nation's food producers.

An alternative to engaging in extensive field experimentation is the use of mathematical modeling. New and effective management practices can be developed and tested by comparing environmental impacts that result from alternative pesticide management methods. However, before models will become useful in this capacity, it is necessary to understand and be able to predict all of the important routes of transport and dissipation.

In a previous paper, Yates (8) reported on a field experiment conducted to measure the volatilization rate of triallate (S-(2,3,3-trichloroallyl) diisopropenyl thiocarbamate) after application to a bare soil. Triallate is a selective pre-

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emergence herbicide used to control wild oats in wheat, barley, and a number of other crops. Triallate has relatively low water solubility and long field half-life, and thus, effective weed control can be maintained for up to 6 months. However, triallate also has a relatively high vapor pressure so that losses to the atmosphere can be an important route of dissipation, unless properly managed.

A simulation model was developed to predict the fate of triallate, or other volatile pesticides, in a saturated and unsaturated soil for varying environmental conditions. The model simulates water, heat, and chemical transport and can also be used to predict the rate of volatilization from the soil surface. The model has been used to successfully simulate volatilization of methyl bromide after application at 25 cm and covering the soil surface with plastic film cover (12).

The purpose of this paper is to test the predictive accuracy of the model by comparison to the measured rate of volatilization observed in a field experiment (8). To do this, four scenarios were simulated, representing different levels of complexity in characterizing the volatilization boundary condition. The first scenario (a) uses the same mathematical formulation as the behavior assessment model (9) and is based on stagnant boundary layer theory. This represents the simplest approach and requires the fewest input parameters. The model assumes isothermal conditions, uniform water flow (e.g., evaporation), and a volatilization boundary condition that remains constant. The second scenario (b) investigates the effects of limited solubility on triallate fate for isothermal conditions. The third scenario (c) allows solar-induced temperature-dependent soil and environmental conditions and simulates water, heat, and chemical transport. The volatilization boundary condition has a similar mathematical formulation as (a) but is now temperature dependent. The fourth scenario (d) uses a volatilization boundary condition that couples soil and micrometeorological conditions (7). All simulations were conducted in a predictive mode with the model parameters determined from independent measurements or literature values. Although model calibration would likely improve comparisons between measured and simulated volatilization, a calibration would not test the predictive capability of the models and boundary conditions.

## Methods

A complete description of the experimental methods is given by Yates (8). The field site was located at the University of California's Moreno Valley Field Station. The soil type was a Greenfield sandy loam containing about 1% organic matter. A circle with a 30 m radius was treated with the pesticide triallate at 8.75 kg ha<sup>-1</sup> in 151.4 L of water. Wauchope et al. (13) reports that triallate has a field dissipation half-life of approximately 100 d; a solubility in water of 4 mg L<sup>-1</sup>; a Henry's law constant,  $K_h = 0.00045$  (20 °C); and an organic carbon distribution coefficient,  $K_{oc} = 2400$  cm<sup>3</sup> g<sup>-1</sup>. The pesticide was applied to the surface of the field using a tractor-mounted sprayer. The initial soil water content of the field was approximately 0.125 (cm<sup>3</sup> cm<sup>-3</sup>) with a porosity of 0.39. The initial concentration (3.5 mg cm<sup>-3</sup>) and depth of application (0.025 cm) was determined by estimating the fluid penetration depth from the application spray volume assuming piston displacement.

The experiment measured surface dissipation and volatilization of triallate for 6 days and provides the experimental data. For each sampling period, the average and standard deviation of three volatilization measurements were calculated and used to compare to simulated values. Soil samples were collected to obtain the initial triallate mass (8.75 kg ha<sup>-1</sup>) and the mass remaining at the end of the experiment (~6 kg ha<sup>-1</sup>). Approximately 31% of the triallate volatilized from the soil.

**Simulation Model.** The numerical model simulates partitioning, degradation, vapor diffusion, liquid dispersion of triallate in soil, and volatilization into the atmosphere. The model can simultaneously solve three partial differential equations for nonlinear transport of water, heat, and solute in a variably saturated porous medium and a first-order degradation process. A more complete description of the model, including the governing equations, can be found in the Supporting Information.

A volatile organic chemical like triallate can be associated with the water, soil, gaseous, and stagnant (e.g., precipitated) phases. The partitioning is assumed to obey the following rules

$$C_G = K_h C_L \quad \text{Henry's law, liquid-vapor partitioning} \quad (1)$$

$$C_S = K_d C_L \quad \text{equilibrium adsorption, liquid-solid partitioning} \quad (2)$$

where  $C_L$ ,  $C_G$ , and  $C_S$ , respectively, are the liquid phase, gas phase, and sorbed triallate concentrations;  $K_h$  is the Henry's law constant (dimensionless), and  $K_d$  is the linear equilibrium sorption coefficient (cm<sup>3</sup> g<sup>-1</sup>).

For situations where a chemical is applied at a concentration that exceeds the solubility limit in water, the maximum aqueous concentration is the liquid solubility,  $C_{sol}$ , that is

$$C_L = \min \left[ \frac{C_{sol}}{C_L} \right] \text{ solubility limits} \quad (3)$$

A simplified methodology was employed to address situations when the chemical concentration exceeds the solubility in water. At any point in the simulation domain where the aqueous concentration is higher than the solubility limit, the excess chemical is instantaneously partitioned into a nonparticipating phase,  $C_p$ . This phase is not explicitly defined, and no distinction is made whether the chemical has precipitated, formed micelles, or has any other physical-chemical manifestation. Therefore, the model treats  $C_p$  as a stored chemical that does not directly participate in the transport process. As the aqueous-phase concentration drops below the solubility limit,  $C_p$  repartitions to the aqueous phase up to the solubility limit; and this continues until  $C_p$  is depleted. An advantage of this approach is that it provides a similar level of simplification as Henry's law and equilibrium adsorption and minimizes the data input requirements; a very important consideration when using a model for predictive purposes.

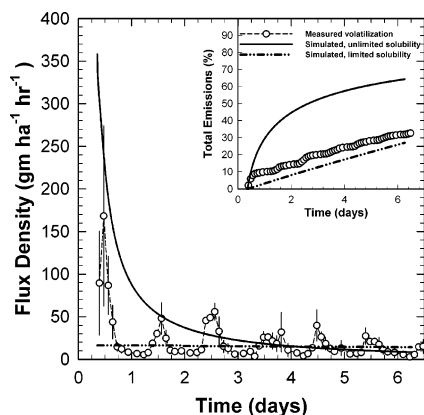
**Volatilization Boundary Condition.** Volatilization at the soil-atmosphere boundary is described using (12)

$$-D_e \frac{\partial C_L}{\partial z} + q C_L|_{z=0} = -h(C_G - C_{atm})|_{z=0} \quad (4)$$

where  $D_e$  is the effective soil dispersion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $q$  is the flux density of water (cm s<sup>-1</sup>),  $h$  is a mass transfer coefficient (cm s<sup>-1</sup>) characterizing chemical transport across the soil surface and into the atmosphere, and  $C_{atm}$  is the chemical concentration in the atmosphere and is assumed zero in the simulations described below. The mass transfer coefficient,  $h$ , is a critical parameter that characterizes the resistance to a chemical crossing the soil-atmosphere boundary. The most common method for expressing  $h$  relies on stagnant boundary layer theory (9)

$$h = \frac{D_{G,air}}{b} \quad (5)$$

where  $D_{G,air}$  is the binary diffusion coefficient for the chemical in air (cm<sup>2</sup> s<sup>-1</sup>), and  $b$  is defined as the thickness of the stagnant boundary layer (cm).



**FIGURE 1. Measured (circles) and predicted (lines) triallate flux density ( $\text{g ha}^{-1} \text{h}^{-1}$ ) after spray application to bare soil. The solid line places no limits on triallate solubility in water; the dashed-dot-dot line uses an aqueous solubility value of  $4 \text{ mg L}^{-1}$  (13).**

Triallate volatilization can be coupled to atmospheric processes by expressing  $h$  in terms of atmospheric resistance terms. This yields a more complex expression for calculating the mass transfer coefficient (7)

$$h = \frac{u^*}{7.3 Re^{1/4} Sc^{1/2} + \left(\frac{U_r}{u^*} - 5\right) \Phi_m} \quad (6)$$

where  $Re$  and  $Sc$ , respectively, are the roughness Reynolds and Schmidt numbers,  $u^*$  is the friction velocity ( $\text{cm s}^{-1}$ ),  $U_r$  is the wind speed at the measurement height ( $\text{cm s}^{-1}$ ), and  $\Phi_m$  is an atmospheric stability correction (14). The denominator of eq 6 consists of two atmospheric resistance terms, one representing diffusive resistance near the surface and the other aerodynamic resistance from the diffusive layer to the measurement height. To use eq 6, several meteorological measurements are needed including gradients of wind speed and temperature.

## Results and Discussion

**Measured Volatilization of Triallate.** Shown in Figure 1 is a time series (circles) of the triallate flux density (i.e., volatilization rate) during the experiment (8). Each point represents the average of the three methods used to measure volatilization. Averaged flux densities were used to compare with the simulated outcomes in an attempt to reduce experimental uncertainty, since it has been reported that the uncertainty in flux measurements can exceed 50% (15), and, therefore, averages should remove some of this uncertainty. The vertical lines indicate the standard deviation of the volatilization measurements at each time point. The curve shows a cyclic behavior with peak rates occurring predominately during the daytime and lower values at night. The maximum averaged daily volatilization rate occurred on the first day and was approximately  $168 \text{ g ha}^{-1} \text{h}^{-1}$ . After the first day, the peak daily volatilization rate was generally less than  $50 \text{ g ha}^{-1} \text{h}^{-1}$ . The minimum averaged daily volatilization rates were  $<10 \text{ g ha}^{-1} \text{h}^{-1}$ .

Also shown in Figure 1 (inset) is the measured total emission (circles). This curve reveals the cumulative mass lost as a percentage of applied triallate during the experiment. The diurnal variation in emission rate is expressed in the total emissions curve as the small cycles superimposed on the trend of this curve. At early times, the curve has a steep slope, indicative of high volatilization rates. After a few hours, the curve has a more linear behavior with smaller slope.

**Scenario 1: Predicted Emissions for Isothermal Conditions.** Assuming isothermal conditions, a very simple model

can be used to simulate the volatilization process. This simplification is often adopted because it leads to less rigorous data requirements and still can yield useful information. For example, a similar model was used to compare simulated and measured triallate volatilization from laboratory columns for evaporative and nonevaporative conditions and good agreement was observed for both volatilization rates and soil concentrations (16).

Models that assume isothermal conditions, in general, have flux density curves that decrease monotonically in a similar manner as shown by the solid line in Figure 1. Comparing the simulated and measured field volatilization rates demonstrates that ignoring ambient temperature variations can result in large deviations from the measured flux-density values. For this case, the simulation significantly overestimates the measured volatilization rate during the first few days of the study but more closely matches the daily average volatilization rate toward the end of the experiment. The model predicts a higher initial period-averaged triallate loss rate ( $251 \text{ g ha}^{-1} \text{h}^{-1}$ ) from soil than was measured ( $168 \text{ g ha}^{-1} \text{h}^{-1}$ ) during the experiment, and the predicted total emissions was 64%.

In a previous study (12), the cumulative emissions for methyl bromide were similar irrespective of assuming isothermal or variable temperature conditions, provided that the same average temperature was used in both simulations. In Figure 1 (inset), however, it is clear that measured cumulative volatilization rate does not behave in a similar manner as predicted and fails to have a curvilinear shape. For this study, the measured cumulative volatilization was approximately linear over the measurement period, and the simple isothermal model does not provide a correct description of the measured total emissions.

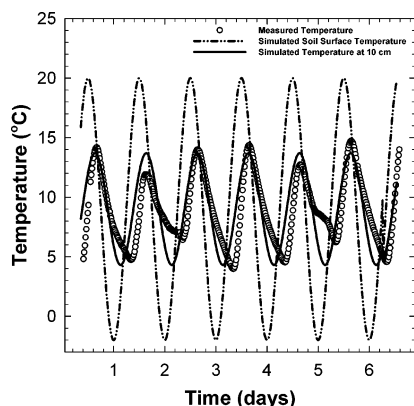
This discrepancy is due to the high concentration levels that occurred in the soil as a result of applying triallate in a relatively small amount of water. Using the measured soil bulk density ( $1.65 \text{ g cm}^{-3}$ ), porosity (0.39), and the volume of applied water ( $0.151 \text{ m}^3$ ), the initial liquid-phase concentration would be nearly 29 times higher than the water solubility. Therefore, an accurate simulation requires addressing solubility effects on triallate fate and transport.

**Scenario 2: Predicted Emissions for Isothermal Conditions and Limited Solubility.** For this example, the only change compared to scenario 1 was that the aqueous-phase concentration was not allowed to exceed the solubility of triallate in water. It is clear in Figure 1 (dashed-dot-dot line) that limiting aqueous concentration to solubility drastically reduces the maximum flux density, which for this example was approximately  $16 \text{ g ha}^{-1} \text{h}^{-1}$ . This is much less than the measured flux density and the value predicted when solubility is not limited (solid line). This simulation provides a better match to the daily average volatilization rate compared to scenario 1 but does not accurately depict the diurnal cycles in the volatilization rate.

Limiting the solubility alone, however, is not sufficient to produce a realistic volatilization curve. This volatilization rate appears to produce a reasonable average behavior but does not accurately predict the daily high and low values. Since the liquid-phase concentrations at the soil surface remain fairly constant under isothermal conditions, the simulated volatilization rate does not vary considerably.

The solubility limits appear to capture the behavior of the cumulative volatilization shown in Figure 1 (inset). The predictions have the observed linear trend, nearly the same slope, and approximately the same value at the end of the experiment (27%). The simulated total emission curve is offset below the measured values mostly due to an underprediction of the average flux behavior during the first few sampling periods. If the model predicted these values more accurately, the measurements and solubility-limited simulation would



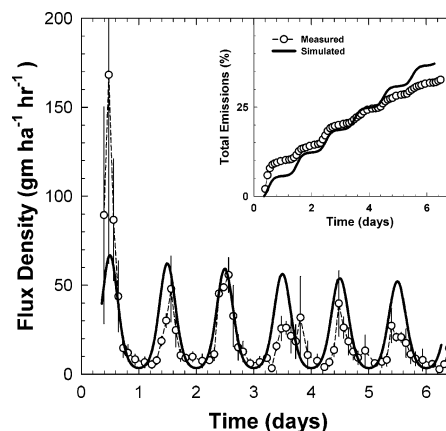


**FIGURE 2.** Measured (circles) and simulated soil temperature at 10 cm (solid line) using the observed mean daily temperature of 9 °C and amplitude of 11 °C. The dashed-dot-dot line is the predicted surface temperature. The Supporting Information has information on the heat transport model.

agree (data not shown) more closely. These results support the use of eq 3 to simulate this experiment, and this approach should provide a more accurate prediction whenever herbicides are applied at concentrations that exceed the aqueous-phase solubility. The remaining simulations use the solubility-limited model since it provides a more appropriate description of the events that occurred during the field study.

**Transport of Heat.** Many soil-chemical properties are affected by ambient temperature. For example, the Henry's law constant and the gas-phase diffusion coefficient for triallate increase with ambient temperature (see the Supporting Information). Clearly, diurnal temperature variations affect the volatilization process, and more accurate volatilization rates should be possible by incorporating temperature variations into the simulation. Shown in Figure 2 are measured and simulated temperature distributions at a depth of 10 cm below the soil surface and the simulated temperature at the soil surface. The soil temperature varied from a few degrees below 0 °C to nearly 20 °C during the midday. At a depth of 10 cm, the temperature cycles were slightly damped ranging from 4 to 15 °C. The temperature model produces a diurnal temperature pattern that predicts the overall soil temperature fairly well, with the exception of the temperature shortly after midnight when the temperature may be underpredicted by as much as 3 °C. It is clear that temperature variations are significant in large-field experiments. Temperature variations can influence some fate and transport parameters producing significant diurnal cycles. For the temperature range observed during this experiment, the Henry's law constant varied by as much as 72%, and the binary diffusion coefficient varied by as much as 16%. These variations could have a significant effect on the volatilization process.

**Scenario 3: Predicted Emissions for Variable Temperature Conditions.** By simulating heat transport, the numerical model can be used to study the effect of diurnal temperature changes on the mass transfer and soil diffusion coefficients. The combined effect of limiting aqueous-phase concentration to the solubility and allowing temperature-induced changes on the mass transfer coefficient is evident in Figure 3. The first day the simulated peak volatilization rate ( $67 \text{ g ha}^{-1} \text{ h}^{-1}$ ) underestimated the measured rate. Beginning on the second day, the diurnal variation of the volatilization rate more closely matched the measured values. During this time, the simulated volatilization rate tended to overestimate the measured peak daily volatilization rate but generally falls within the error bars of the measurements. Exceptions to this occur on days 4 and 6 where the predicted peak value falls outside the error bars.



**FIGURE 3.** Measured (circles) and predicted (lines) triallate flux density ( $\text{g ha}^{-1} \text{ h}^{-1}$ ) after spray application to bare soil. The solid line is the predicted flux density using an aqueous solubility value of  $4 \text{ L}^{-1}$  and includes the effect of temperature on the mass transfer and binary diffusion coefficients. Resistance to volatilization was modeled using a stagnant boundary layer.

The predicted cumulative emission (37%) produces a curve that deviates slightly from the measurements and has a greater slope. Although the predicted curve appears to match the measurements during the 6-day period, extrapolating beyond indicates an increasing deviation between predictions and measurements. There appears to be no advantage using a more complex, temperature-dependent, simulation to obtain this information. There was little improvement compared to scenario 1, which underestimated early emissions but, thereafter, had nearly identical slopes.

Visual inspection of Figure 3 and noting the model performance statistics listed in Table 1 demonstrates that this simulation provided a better overall description of the triallate flux density. The quantitative measures of model performance reveal the importance of the assumptions adopted in the modeling, i.e., isothermal behavior, limits on solubility, etc. Several of the methods presented in Table 1 use an analysis of residual error between the model and measured outcomes to rank model performance. These include the root mean squared error (RMSE), coefficient of determination (CD), and the efficiency factor (EF) (17). For a model that accurately predicts the measured values, the RMSE, CD, and EF, respectively, should have values close to 0, 1, and 1. Another approach is based on a graphical comparison that makes use of a regression line between simulated and measured flux density values. A simulation that predicted the measured values perfectly would have a (1:1) regression line with a slope, intercept, and  $r^2$ , respectively, of 1, 0, and 1.

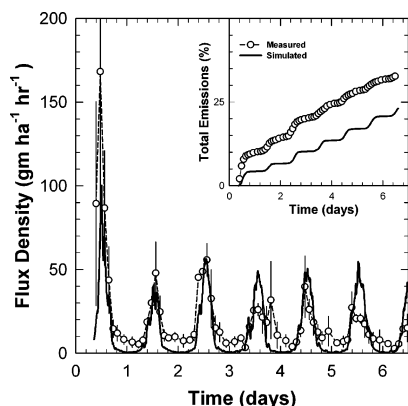
For each measure in Table 1, the result that is closest to the optimal value is shown in bold. Scenario 3, which appears more accurate based on visual inspection of Figure 3, was found to have the most accurate test statistics for 2 of the 6 performance measures. This compares with zero for scenarios 1 and 2 and provides quantitative evidence that the model in scenario 3 provides a superior simulation of the volatilization process compared to scenarios 1 and 2.

**Scenario 4: The Effect of Coupling Soil and Atmospheric Processes on Predicted Emissions.** The smooth and nearly sinusoidal simulated volatilization rate in Figure 3 is a direct consequence of the simulated soil temperatures (Figure 2), since the resistance to transport across the surface boundary controls the volatilization rate and depends strongly on temperature. In general, measured volatilization rates are not as smooth as those simulated in scenario 3 (4, 7, 8, 15). There are other processes that affect the volatilization rate, such as, the atmospheric stability, turbulent mixing, and

**TABLE 1. Quantitative Measures of Model Performance for Each Scenario<sup>a</sup>**

	constant temperature		variable temperature	
	scenario 1	scenario 2	scenario 3	scenario 4
root mean squared error, [–]	2.14	1.22	0.92	<b>0.82</b>
coefficient of determination, [–]	0.19	14.9	<b>1.72</b>	1.80
efficiency factor, [–]	–2.22	–0.05	0.40	<b>0.52</b>
regression line (1:1)				
slope of regression, [–]	0.33	13.00	0.89	<b>1.10</b>
intercept, [gm ha <sup>–1</sup> h <sup>–1</sup> ]	8.28	–176.35	–1.73	5.24
r <sup>2</sup> , [–]	0.50	0.12	0.44	<b>0.59</b>

<sup>a</sup> Root mean squared error:  $[1/n \sum (M_i - P_i)^2 / \sum M_i^2]$ , coefficient of determination:  $\sum (M_i - \bar{M})^2 / \sum (P_i - \bar{M})^2$ , efficiency factor:  $[\sum (M_i - \bar{M})^2 - \sum (P_i - \bar{M})^2] / \sum (M_i - \bar{M})^2$ . M - measurements, P - model predictions.



**FIGURE 4. Measured (circles) and predicted (lines) triallate flux density (g ha<sup>–1</sup> h<sup>–1</sup>) after spray application to bare soil. The solid line is the predicted flux density using an aqueous solubility value of 4 L<sup>–1</sup> and includes the effect of temperature. The volatilization boundary condition was coupled to atmospheric processes.**

spatial variability that were not addressed with the simple stagnant boundary layer model used in scenario 3 but can be addressed by coupling soil and atmospheric processes.

A simulation that uses eq 6 requires temperature and wind speed data during the simulated period, which were obtained during the field experiment. Shown in Figure 4 are the predicted triallate volatilization rates that result from coupling soil and atmospheric processes. The predicted peak rate (100 g ha<sup>–1</sup> h<sup>–1</sup>) underestimates the measured rate but is the most accurate of all the simulations. It is clear that atmospheric conditions can affect the volatilization rate, tends to produce flux density values with significant fluctuations, and appears to produce more accurate emission predictions. Similar results were observed simulating field-scale methyl bromide emissions (12). The additional micrometeorological information produces a flux density curve that has commonly observed erratic variations. This is caused by relatively rapid changes in the wind speed and the atmospheric stability parameter and suggests that the effect of ambient temperature and meteorological conditions are important.

Although coupling of atmospheric processes to the mass transfer coefficient produces a more realistic emission rate, the total emissions (21%) appear to be somewhat less accurate than the other cases. The slope of the predicted cumulative emissions appears to be approximately the same as the measured values, but there is an offset due to inaccurately predicting the emission rate during the first 3 sampling periods and an underprediction of the flux density at night. This latter discrepancy could be corrected by placing a lower limit on the mass transfer coefficient (see Figure 3), but the appropriate information would have to be available a priori

**TABLE 2. Total Soil Concentration at the End of the Experiment.**

depth range (cm)	measured total concn, <sup>a</sup> gm cm <sup>–3</sup>	simulated total concn, gm cm <sup>–3</sup>			
		scenario 1	scenario 2	scenario 3	scenario 4
0–3	21.1 ± (6.2)	9.76	21.8	18.4	22.4
3–6	0.86 ± (0.55)	0	0	0	0
6–9	0.38 ± (0.51)	0	0	0	0
9–12	0.41 ± (0.51)	0	0	0	0

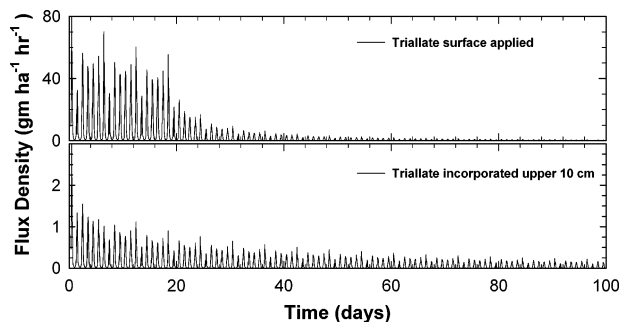
<sup>a</sup> ± (SD).

to allow the simulation to be conducted in a predictive mode. Additional study is needed to develop improved methods for simulating the early time behavior.

Including micrometeorological information into simulations of the volatilization rate provides more accurate and realistic emissions as shown in Table 1. For this scenario, 4 of 6 test statistics have model-performance values closest to the optimum, compared to only 2 for scenario 3. Although this approach requires considerably more information about atmospheric processes, this may be justified when the rate of the volatilization rate over short periods is of interest. It also seems that for studies where the intended information is the cumulative or total emissions, a simulation using micrometeorological data may not be justified because simple boundary conditions (e.g., scenario 2) were found to be accurate.

**The Distribution of Triallate in Soil.** A simulation can also be used to predict the triallate concentration in the soil. Shown in Table 2 is the area averaged triallate concentration in the soil at the end of the experiment, where a concentration of 21.1 g cm<sup>–3</sup> was measured in the upper 3 cm. This represents nearly 93% of the total remaining mass, with very low levels measured between 3 and 12 cm depth. The simulated triallate concentration in the upper 3 cm was 22.4 g cm<sup>–3</sup> (scenario 4) and is similar in value to the measurement. However, the simulation indicates that triallate should not have moved beyond a depth of 3 cm, although the measurements indicate that some triallate was present. It is unlikely that the measured values below 3 cm was due to solute transport, since no irrigation water was applied to the soil after application. Two other possible explanations are vapor diffusion into the subsurface or, more likely, contamination during sampling. Care was taken to remove the soil cores without contaminating deeper samples, but even with precautions, some smearing of soil containing triallate to deeper depths is possible.

**Predicting Emissions after Soil Incorporation.** A significant advantage of using models to study pesticide management is the relative ease and low expense obtaining new and potentially important information. For example, a



**FIGURE 5. Predicted triallate volatilization after surface spray application (A) and after incorporation (B) uniformly into soil to a depth of 10 cm.**

relatively simple method to reduce triallate emissions is soil incorporation. Incorporating triallate into the upper 10 cm of soil under the same conditions described in scenario 4 reduces emission from 80% to <5% after 100 d (see Figure 5). Further, the triallate remaining in the soil after 100 d for surface and incorporated applications, respectively, was 6% and 41% of the applied material (i.e., 8.75 kg ha<sup>-1</sup>). This indicates that soil herbicide concentrations are maintained much longer compared to surface application and, thus, may significantly increase pesticide efficacy and reduce environmental risk. Obtaining the same information from experimentation would be orders of magnitude more costly, and the information used for comparison would not allow isolation of solely the surface-application/10 cm-incorporation effect. It is also virtually impossible in outdoor field settings to conduct side-by-side experiments that have the same soil and environmental conditions and that do not produce interferences between study sites. Therefore, modeling should be included as an important component of regulatory decision-making to protect the atmosphere from pesticide emissions.

### Acknowledgments

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### Supporting Information Available

Description of the transport equations, method of solution, and testing. This material is available free of charge via the Internet at <http://pubs.acs.org>.

### Literature Cited

- (1) U.S. EPA. *Agricultural chemicals in ground water: Proposed pesticide strategy*; Office of Pesticides and Toxic Substances: Dec, 1987; 150 pp.

- (2) McConnell, L. L.; Harman-Fetcho, J. A.; Hagy, J. D. Measured concentrations of herbicides and model predictions of atrazine fate in the Patuxent River Estuary. *J. Environ. Qual.* **2004**, *33*, 594–604.
- (3) van den Berg, F.; Kubiak, R.; Benjey, W.; Majewski, M.; Yates, S. R.; Reeves, G.; Smelt, J.; van der Linden, A. Emission of pesticides into the air. *Water, Air, Soil Pollut.* **1999**, *115*, 195–218.
- (4) Prueger, J. H.; Gish, T. J.; McConnell, L. L.; McKee, L. G.; Hatfield, J. L.; Kustas, W. P. Solar radiation, relative humidity, and soil water effects on metolachlor volatilization. *Environ. Sci. Technol.* **2005**, *39*, 5219–5226.
- (5) Cryer, S. A. Predicting soil fumigant air concentrations under regional and diverse agronomic conditions. *J. Environ. Qual.* **2005**, *34*, 2197–2207.
- (6) U.S. EPA. *Registration Eligibility Decision for Triallate*; EPA-738-R-00-021 (March 2001); Office of Pesticide Programs, U.S. Environmental Protection Agency: Washington, DC 20460, 2001; 246 pp.
- (7) Baker, J. M.; Koskinen, W. C.; Dowdy, R. H. Volatilization of EPTC: simulation and measurement. *J. Environ. Qual.* **1996**, *25*, 169–177.
- (8) Yates, S. R. Measuring herbicide volatilizations from bare soil. *Environ. Sci. and Technol.* **2006**, *40*, 3223–3228.
- (9) Jury, W. A.; Spencer, W. F.; Farmer, W. J. Behavior assessment model for trace organics in soil: 1. Model description. *J. Environ. Qual.* **1983**, *12*, 558–564.
- (10) Rao, P. S. C.; Hornsby, A. G.; Jessup, R. E. Indexes for ranking the potential for pesticide contamination of groundwater. *Soil Crop Sci. Soc. Fla. Proc.* **1985**, *44*, 1–8.
- (11) Loague, K.; Yost, R. S.; Green, R. E.; Liang, T. C. Uncertainty in a pesticide leaching assessment for Hawaii. *J. Contam. Hydrol.* **1989**, *4*, 139–161.
- (12) Yates, S. R.; Wang, D.; Papiernik, S. K.; Gan, J. Predicting pesticide volatilization from soils. *Environmetrics* **2002**, *13*, 569–578.
- (13) Wauchope, R. D.; Buttler, T. M.; Hornsby, A. G.; Augustijn-Beckers, P. W. M.; Burt, J. P. The SCS/ARS/CES Pesticide properties database for environmental decision-making. *Rev. Environ. Contamin. Toxicol.* **1992**, *123*, 1–155.
- (14) Rosenberg, N. J.; Blad, B. L.; Verma, S. B. *Microclimate, The biological environment*; John Wiley & Sons: New York, 1983; 495 pp.
- (15) Majewski, M. S. Error evaluation of methyl bromide aerodynamic flux measurements. In *Fumigants: Environmental Fate, Exposure, and Analysis*; Seiber, J. N., Knuteson, J. A., Woodrow, J. E., Wolfe, N. L., Yates, M. V., Yates, S. R., Eds.; ACS Symp. Ser. 652, American Chemical Society: Washington, DC, 1997; pp 135–153.
- (16) Jury, W. A.; Grover, R.; Spencer, W. F.; Farmer, W. J.; Modeling vapor losses of soil-incorporated triallate. *Soil Sci. Soc. Am. J.* **1980**, *44*, 445–450.
- (17) Loague, K.; Green, R. E. Statistical and graphical methods for evaluating solute transport models: Overview and application. *J. Contam. Hydrol.* **1991**, *7*, 51–73.

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